

Chemistry of $\text{Et}_3\text{P}\cdot\text{CS}_2$ Metal Complexes: Synthesis of 1,1-Dithiolate Complexes via Nucleophilic Attacks on $[(\text{triphos})\text{Co}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$. X-ray Structure of $[(\text{triphos})\text{Co}(\text{S}_2\text{CO})]$

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The synthesis of the 1,1-dithiolate cobalt(II) complexes $[(\text{triphos})\text{Co}(\text{S}_2\text{C}(\text{H})\text{PEt}_3)]\text{BPh}_4$ (2), $[(\text{triphos})\text{Co}(\text{S}_2\text{CO})]$ (3), and $[(\text{triphos})\text{Co}(\text{S}_2\text{CS})]$ (4) (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) via the reaction of complex $[(\text{triphos})\text{Co}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$ (1) with nucleophiles has been described. All the complexes have been characterized by appropriate physical methods. The molecular structure of 3 has been determined from counter diffraction data. Crystal data for 3: $a = 20.294$ (8) Å, $b = 17.954$ (7) Å, $c = 10.218$ (4) Å, orthorhombic, space group $Pn2_1a$, $Z = 4$. The structure was refined by full-matrix least-squares techniques to R and R_w of 0.063 and 0.055, respectively. The cobalt atom is five-coordinated by the three phosphorus atoms of the triphos ligand and by the two sulfur atoms of the dithiocarbonate group in a distorted-square-pyramidal environment.

Introduction

In recent papers the coordinative behavior of the triethylphosphine-carbon disulfide adduct, $\text{Et}_3\text{P}\cdot\text{CS}_2$, has been widely described.¹⁻³ Indeed this molecule exhibits various anchoring modes to metals, behaving as an η^1 , η^2 , or η^3 ligand (Figure 1).

Among the complexes obtained, those containing the zwitterion $\text{Et}_3\text{P}\cdot\text{CS}_2$ as a bidentate ligand, have aroused our interest since a metal ion, when chelated, often causes the electrons in a ligand to be redistributed, and as a result, the reactivity at some point in the chelate ring is altered to some extent. On the other hand it has been extensively reported that dithio acid metal complexes such as xanthates, dithiocarbamates, and trithiocarbonates may undergo nucleophilic attack on the carbon atom of the $-\text{CS}_2$ group.^{6,7}

With this in mind, we have investigated the reactivity of the complex $[(\text{triphos})\text{Co}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$ (1) (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) toward various nucleophiles. The reactions performed are summarized in Scheme I; some of them represent a novel and potentially useful route to metal complexes with ligands such as S_2CO^{2-} and $\text{S}_2\text{C}(\text{H})\text{PEt}_3^-$, which do not exist in the free form.

All complexes have been characterized and their physical properties studied by the usual methods. A complete X-ray structure determination has been carried out on the complex $[(\text{triphos})\text{Co}(\text{S}_2\text{CO})]$ (3).

A preliminary account of part of this work has already been published.⁸

Experimental Section

Compound 1 was prepared according to a published procedure.⁸ Tetrahydrofuran was dried by refluxing over LiAlH_4 , before distillation. All other chemicals and organic solvents employed were reagent grade and were used without further purification.

Preparation of the Complexes. All reactions were routinely performed in an atmosphere of dry nitrogen except where stated otherwise.

The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of dry nitrogen.

$[(\text{triphos})\text{Co}(\text{S}_2\text{C}(\text{H})\text{PEt}_3)]\text{BPh}_4$ (2). A solution of NaBH_4 (0.7 mmol) in ethanol (20 mL) was added to a suspension of 1 (0.5 mmol) in CH_2Cl_2 (30 mL). The suspended solid dissolved to give an orange-brown solution. Orange-brown crystals were obtained on addition of ethanol and slow evaporation of the solvent. They were recrystallized from acetone and butanol. Conductivity: $45 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for $\text{C}_{72}\text{H}_{73}\text{BCoP}_3\text{S}_2$: C, 72.17; H, 6.31; Co, 4.91; P, 10.34. Found: C, 72.02; H, 6.26; Co, 4.83; P, 10.31.

$[(\text{triphos})\text{Co}(\text{S}_2\text{CO})]$ (3). Sodium metal (2 mmol) was allowed to react completely with 20 mL of ethanol, and the resulting solution of sodium ethoxide was slowly added to a suspension of 1 (0.5 mmol) in THF (30 mL) until it dissolved to give a red-violet solution. Dioxxygen was then bubbled until the color changed to yellow-green. After concentration of the resulting solution, yellow-green crystals were obtained, which were recrystallized from CH_2Cl_2 and ethanol. 3 can also be obtained by exposing a CH_2Cl_2 /ethanol solution of 2 to the air. Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{CoP}_3\text{S}_2$: C, 65.02; H, 5.06; Co, 7.59. Found: C, 64.97; H, 5.03; Co, 7.58.

$[(\text{triphos})\text{Co}(\text{S}_2\text{CS})]$ (4). A solution of sodium ethoxide, prepared as above, was slowly added to a suspension of 1 (0.5 mmol) in THF (30 mL) until complete dissolution. A large excess of sulfur in boiling THF (20 mL) was then added. On addition of butanol (20 mL), red crystals precipitate, which were recrystallized from CH_2Cl_2 and butanol. Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{CoP}_3\text{S}_3$: C, 63.70; H, 4.96; Co, 7.44; S, 12.14. Found: C, 63.72; H, 4.93; Co, 7.40; S, 12.09.

$[(\text{triphos})\text{Co}(\pi\text{-CS}_2)]$ (5). A suspension of 1 (0.3 mmol) and sodium sand (1.5 mmol) in THF (30 mL) was stirred at room temperature until a deep red solution was obtained (about 2 h) and then stirred for a further 30 min. Butanol (20 mL) was then added to the filtered solution. Dark red crystals formed on standing.

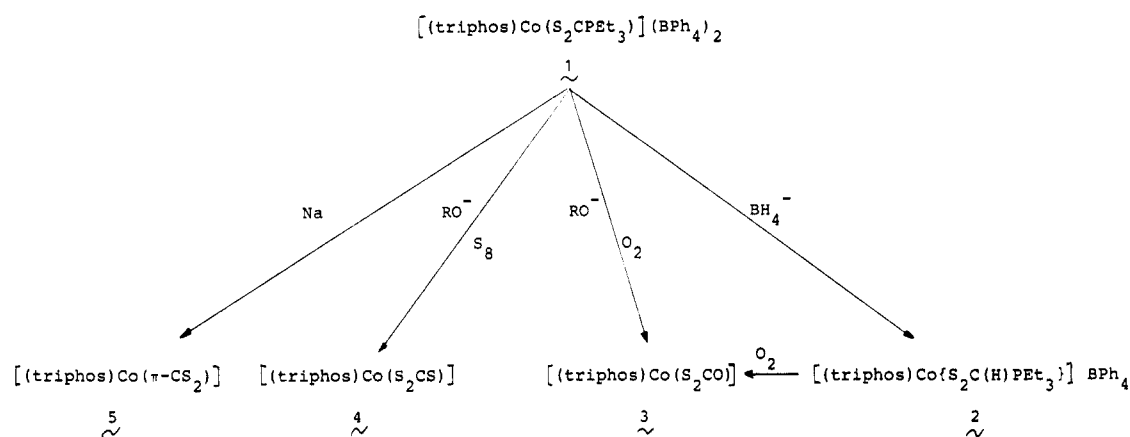
Physical Measurements. Infrared spectra were obtained as Nujol mull with a Perkin-Elmer 283 spectrophotometer. The methods used for the magnetic measurements and the recording of the UV-visible spectra have been described previously.⁹ Conductance measurements were made with a WTW Model LBR/B conductivity bridge in ca. 10^{-3} M nitroethane solutions.

Collection and Reduction of X-ray Intensity Data. A yellow-green prism of approximate dimensions $0.1 \times 0.2 \times 0.3$ mm was selected for data collection on a Philips PW 1100 diffractometer, by using $\text{Mo K}\alpha$ ($\lambda = 0.7107$ Å) graphite-monochromated radiation. The crystals are orthorhombic and belong to space group $Pn2_1a$, as inferred from the systematic absences $0kl$ for $k + l = 2n + 1$ and $h00$ for $h = 2n + 1$, with four molecules in the unit cell. Cell dimensions, determined by least-squares refinement of the angular settings of 20 carefully centered reflections, are $a = 20.294$ (8) Å, $b = 17.954$ (7) Å, $c = 10.218$ (4) Å, and $V = 3723.0$ Å³. The calculated density is 1.384 g cm^{-3} for $Z = 4$. For the intensity collection an ω - 2θ scan

- Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Organometallics* 1982, 1, 778.
- Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* 1981, 219, C13.
- Bianchini, C.; Meli, A.; Orlandini, A.; Scapacci, G. *J. Organomet. Chem.* 1981, 215, C59.
- Bianchini, C.; Innocenti, P.; Meli, A.; Orlandini, A.; Scapacci, G. *J. Organomet. Chem.* 1982, 233, 233.
- Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.*, in press.
- Fackler, J. P., Jr.; Seidel, W. C. *Inorg. Chem.* 1969, 8, 1631.
- Bianchini, C.; Mealli, C.; Meli, A.; Scapacci, G. *J. Chem. Soc. Dalton Trans.* 1982, 799.
- Bianchini, C.; Meli, A.; Orlandini, A. *Angew. Chem. Suppl.* 1982, 471.

(9) Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* 1968, 7, 1417.

Scheme I

Table I. Positional and Thermal Parameters for [(triphos)CoS₂CO]^a

atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co	-527 (2)	-1321	474 (3)	33 (2)	25 (2)	40 (2)	3 (3)	4 (2)	-7 (2)
P1	539 (3)	-1266 (4)	1060 (5)	32 (3)	30 (3)	43 (4)	-6 (4)	-4 (4)	3 (4)
P2	-428 (3)	-178 (3)	-427 (7)	35 (4)	25 (3)	47 (5)	1 (4)	8 (5)	-1 (3)
P3	-850 (3)	-829 (4)	2418 (8)	24 (3)	37 (3)	35 (4)	-6 (4)	4 (4)	-3 (3)
S1	-1509 (3)	-1616 (4)	-430 (9)	45 (4)	53 (4)	96 (6)	-12 (5)	-40 (5)	1 (3)
S2	-546 (4)	-2574 (4)	473 (10)	51 (5)	32 (4)	170 (10)	-7 (6)	-9 (8)	-20 (4)

^a The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Coordinates are multiplied by 10⁴; temperature factors, by 10³. The y coordinate of the Co atom was chosen to have accordance with the isomorphous [(triphos)Co(BH₄)] complex.¹⁵

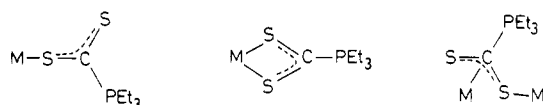


Figure 1.

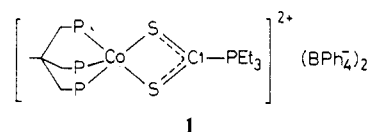
mode was used with a scan width variable with θ , according to the expression $A + B \tan \theta$, where $A = 0.8^\circ$ and $B = 0.69$. A scan speed of $0.06^\circ/\text{s}$ was used. Background counts were made for half of the scan time at each end of the scan. Three control reflections were monitored every 120 min, but no systematic trend was noticed. After correction for background, the standard deviations $\sigma(I)$ of the intensity I were calculated as previously described¹⁰ by using the value of 0.03 for the instability factor k . Intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied, the linear absorption coefficient being $\mu(\text{Mo K}\alpha) = 7.26 \text{ cm}^{-1}$. An empirical estimation of the effect of absorption showed the largest change in intensities within 2%. From a total of 2895 reflections ($5^\circ < 2\theta < 46^\circ$), 1070 were considered observed with $I > 2.5\sigma(I)$. Atomic scattering factors of the neutral atoms were taken from ref 11 for non-hydrogen atoms and from ref 12 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.¹³ The function minimized during the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w are given as $w = 1/\sigma(F_o)^2$. All calculations were carried out by using SHELX-76 crystallographic system, on a SEL 32/70 computer installed in our institute.¹⁴

Solution and Refinement of the Structure. On the assumption that the compound is isomorphous with [(triphos)Co(BH₄)],¹⁵ the final parameters of this structure were used as starting parameters of the present complex. A ΔF Fourier revealed the positions of the S₂CO

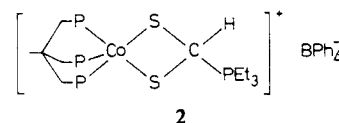
group. Full-matrix least-squares cycles, by assigning isotropic temperature factors to all the non-hydrogen atoms, were followed by mixed cycles, where anisotropic temperature factors were attributed to cobalt, sulfur, and phosphorus atoms. Throughout the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. At this point the hydrogen atoms were introduced in their calculated positions but were not refined. Owing to the polar nature of the $Pn2_1a$ space group, two possible orientations of the structure (x, y, z) and (x, \bar{y}, z) are to be considered. The absolute configuration was determined by applying the anomalous dispersion corrections. A final least-squares cycle led to convergence at the discrepancy factors $R = 0.063$ and $R_w = 0.055$ for (x, y, z) and $R = 0.064$ and $R_w = 0.057$ for (x, \bar{y}, z) , respectively. An analysis of the standard deviations confirmed that the (x, y, z) structure was the correct one. Tables I and II report the final positional and thermal parameters with their estimated standard deviations for all non-hydrogen atoms. A listing of F_o and F_c structure factors is available as supplementary material.

Results and Discussion

It has been recently reported that the C1 carbon atom of **1** has so much electrophilicity as to be able to abstract a



hydride ion from ethanol.⁵ This finding has prompted us to investigate the reactivity of the coordinated Et₃P-CS₂ ligand toward various nucleophiles. Indeed hydride ion attacks the C1 carbon atoms: by reaction of BH₄⁻ anions with **1**, the cobalt(II) derivative [(triphos)Co(S₂C(H)PEt₃)]BPh₄ (**2**) is easily prepared.⁵



In addition to the nucleophilic attack by hydride ion at the C1 carbon atom site, other reactions may occur between **1** and nucleophiles. Indeed all manner of nucleophiles such as OH⁻,

- (10) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 1979
 (11) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99.
 (12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
 (13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.
 (14) Sheldrick, G. M. "System of Computing Programs", University of Cambridge, Cambridge, 1976 (adapted by Dr. C. Mealli).
 (15) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768.

Table II. Positional and Thermal Parameters for [(triphos)CoS₂CO]^a

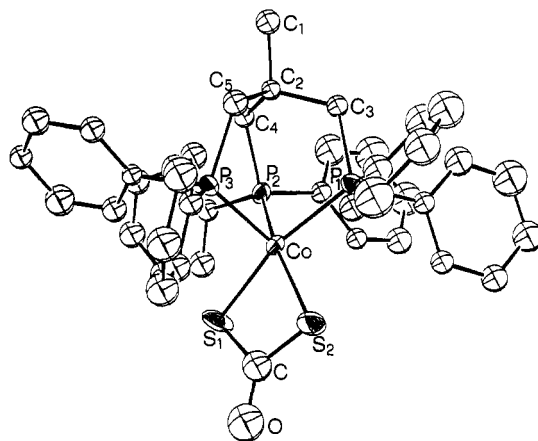
atom	x	y	z	U, Å ²
C1	535 (13)	851 (11)	2723 (22)	44 (6)
C2	215 (10)	189 (11)	1990 (22)	29 (6)
C3	787 (10)	-306 (12)	1500 (23)	34 (7)
C4	-201 (10)	494 (11)	848 (21)	34 (7)
C5	-192 (11)	-218 (13)	3105 (23)	46 (7)
C6	825 (8)	-1792 (8)	2491 (18)	58 (8)
C7	1462 (8)	-1681 (8)	2967 (18)	82 (10)
C8	1684 (8)	-2086 (8)	4045 (18)	82 (10)
C9	1270 (8)	-2603 (8)	4647 (18)	77 (9)
C10	633 (8)	-2714 (8)	4170 (18)	96 (11)
C11	411 (8)	-2309 (8)	3092 (18)	46 (7)
C12	1162 (8)	-1573 (7)	-131 (15)	36 (7)
C13	1741 (8)	-1177 (7)	-375 (15)	63 (8)
C14	2197 (8)	-1447 (7)	-1279 (15)	96 (11)
C15	2075 (8)	-2113 (7)	-1940 (15)	74 (10)
C16	1496 (8)	-2509 (7)	-1697 (15)	55 (8)
C17	1040 (8)	-2239 (7)	-792 (15)	40 (7)
C18	195 (10)	-129 (8)	-1697 (18)	38 (7)
C19	521 (10)	530 (8)	-2017 (18)	85 (10)
C20	971 (10)	541 (8)	-3047 (18)	111 (14)
C21	1096 (10)	-107 (8)	-3758 (18)	99 (12)
C22	770 (10)	-767 (8)	-3439 (18)	61 (8)
C23	319 (10)	-778 (8)	-2408 (18)	37 (6)
C24	-1115 (8)	311 (9)	-1292 (15)	40 (7)
C25	-1255 (8)	1052 (9)	-991 (15)	63 (9)
C26	-1771 (8)	1418 (9)	-1624 (15)	55 (8)
C27	-2147 (8)	1042 (9)	-2557 (15)	64 (8)
C28	-2007 (8)	301 (9)	-2858 (15)	72 (9)
C29	-1491 (8)	-65 (9)	-2225 (15)	60 (8)
C30	-1048 (6)	-1465 (8)	3749 (14)	38 (7)
C31	-779 (6)	-1420 (8)	5003 (14)	42 (7)
C32	-940 (6)	-1953 (8)	5942 (14)	66 (8)
C33	-1370 (6)	-2533 (8)	5627 (14)	67 (8)
C34	-1639 (6)	-2578 (8)	4373 (14)	64 (8)
C35	-1478 (6)	-2044 (8)	3434 (14)	52 (7)
C36	-1562 (7)	-190 (8)	2507 (14)	30 (6)
C37	-1693 (7)	188 (8)	3670 (14)	44 (7)
C38	-2222 (7)	683 (8)	3740 (14)	55 (8)
C39	-2620 (7)	799 (8)	2645 (14)	39 (6)
C40	-2489 (7)	421 (8)	1482 (14)	70 (10)
C41	-1960 (7)	-74 (8)	1412 (14)	47 (8)
C	-1304 (14)	-2526 (15)	-201 (27)	65 (9)
O	-1681 (10)	-3073 (11)	-443 (23)	97 (7)

^a Coordinates are multiplied by 10⁴; temperature factors, by 10³.

RO⁻, S²⁻, RS⁻, and NR²⁻ react with **1** to give red-violet solutions, but no products can be isolated. However, if oxygen is bubbled into these solutions, the color turns yellow-green and crystals of empirical formula [(triphos)Co(S₂CO)] (**3**) are precipitated.

Compound **3** is quite air stable and soluble in chlorinated solvents in which it is nonconducting. The room-temperature μ_{eff} is equal to 1.97 μ_{B} , as expected for a low-spin d⁷ configuration. The electronic spectra, practically identical both in the solid state and in 1,2-dichloroethane solution, show absorption maxima at 10 000 ($\epsilon = 318$), 14 800 ($\epsilon = 333$), 21 050 ($\epsilon = 592$), and 23 550 cm⁻¹ ($\epsilon = 4148$), and are fully comparable with those of distorted five-coordinate cobalt(II) complexes with P₃S₂ donor set.⁷ The IR spectrum in the CO stretching region has two bands at 1690 and 1600 cm⁻¹, which are indicative of a chelate dithiocarbonate ligand.^{6,16}

The crystal and molecular structure of the complex molecule consists of monomeric units of [(triphos)Co(S₂CO)], whose perspective view is given in Figure 2. Selected bond distances and angles are reported in Table III. The metal atom is five-coordinated by the three phosphorus atoms of the triphos ligand and by the two sulfur atoms of the dithiocarbonate

**Figure 2.** Perspective view of the complex molecule [(triphos)Co(S₂CO)] (ORTEP drawing with 30% probability ellipsoids).**Table III.** Selected Bond Distances (Å) and Angles (Deg) for [(triphos)Co(S₂CO)]

Co-P1	2.246 (6)	P2-C18	1.81 (2)
Co-P2	2.259 (6)	P2-C24	1.87 (2)
Co-P3	2.271 (8)	P3-C5	1.87 (2)
Co-S1	2.260 (7)	P3-C30	1.82 (2)
Co-S2	2.250 (6)	P3-C36	1.85 (2)
P1-C3	1.85 (2)	S1-C	1.70 (3)
P1-C6	1.84 (2)	S2-C	1.69 (3)
P1-C12	1.84 (2)	C-O	1.27 (3)
P2-C4	1.83 (2)	Co...C	2.77 (3)
P1-Co-P2	89.0 (3)	Co-P2-C18	113.4 (5)
P1-Co-P3	91.6 (2)	Co-P2-C24	123.5 (6)
P1-Co-S1	165.6 (3)	C4-P2-C18	107.6 (8)
P1-Co-S2	93.5 (3)	C4-P2-C24	102.4 (8)
P2-Co-P3	91.6 (3)	C18-P2-C24	99.1 (9)
P2-Co-S1	97.2 (3)	Co-P3-C5	110.6 (8)
P2-Co-S2	155.5 (4)	Co-P3-C30	118.2 (5)
P3-Co-S1	101.2 (3)	Co-P3-C36	120.7 (6)
P3-Co-S2	112.6 (3)	C5-P3-C30	104.2 (9)
S1-Co-S2	75.5 (3)	C5-P3-C36	100.2 (9)
Co-P1-C3	111.6 (7)	C30-P3-C36	100.4 (7)
Co-P1-C6	119.6 (5)	Co-S1-C	87.3 (10)
Co-P1-C12	118.2 (5)	Co-S2-C	88.0 (10)
C3-P1-C6	101.5 (9)	S1-C-O	124.7 (22)
C3-P1-C12	104.7 (8)	S2-C-O	126.2 (21)
C6-P1-C12	98.9 (8)	S1-C-S2	109.1 (16)
Co-P2-C4	109.3 (7)	Co-C-O	176.3 (21)

ligand in a distorted square-pyramidal environment. The distortion from the limit geometry is evidenced by the values of the P1-Co-S1 and P2-Co-S2 bond angles, 165.6 (3) and 155.5 (4)°, respectively, instead of the ideal 180°. The cobalt atom and the dithiocarbonate ligand are essentially coplanar, the maximum deviation from the least-squares plane being 0.03 Å. The Co-P and the Co-S bond distances, averaging 2.259 (7) and 2.255 (5) Å, respectively, fall in the usual range; a comparison with the corresponding values reported for the [(etriphos)Co(S₂C(H)PEt₃)](BPh₄)₂ complex,⁵ Co-P(av) = 2.200 (3) and Co-S(av) = 2.19 (2) Å, shows an increasing of the bond distances in the coordination sphere, which could be attributed to electronic factors (Co(II) instead of Co(III)) as well as to steric arguments (phenyl groups in the place of ethylenic chains). However, a variety of triphos cobalt complexes with different ancillary ligands is reported, with Co-P bond distances falling in an extremely large range of values.¹⁷ Bond distances and angles within the S₂CO unit well match the values in other dithiocarbonate complexes; the S-C (1.695 (5) Å (average)) and C-O (1.27 (3) Å) bond distances closely resemble those found in the K[Rh(S₂CO)₂(PMe₂Ph)₂]·3H₂O¹⁶

(16) Gould, R. O.; Gunn, A. M.; Van der Hark, T. E. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1714.

(17) Ghilardi, C. A.; Mealli, C.; Midollihi, S.; Nefedov, V. I.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1980**, *19*, 2454 and references therein.

(1.72 Å (average), 1.26 Å (average)) as those reported in the dimeric [(Cp₂V)₂(COS₂)] complex¹⁸ (1.726 Å (average), 1.262 Å), where the dithiocarbonate acts as tridentate bridging ligand. A comparison with the [Pt(S₂CO)(PPh₃)₂] compound,¹⁹ where the phosphine ligands are each trans to the sulfur atoms of the dithiolate group, shows some difference, the S-C (1.78 Å (average)) and C-O (1.19 Å) bond distances in the platinum complex reflecting a larger π -electron withdrawing of the phosphine ligands, allowed by the square-planar geometry. However, the S-C and C-O bond distances, in the present compound, seem to suggest an overall electronic delocalization of the S₂CO group.

Dithiocarbonate complexes are quite rare since they cannot be obtained directly from the ligand, which is unstable to disproportionation. Most of them are prepared from the reaction of metal xanthates with phosphines.^{6,19} The mechanism for this reaction has been suggested to involve the formation of an ionized xanthate, followed by nucleophilic attack of this anion on the alkoxy group of the coordinated xanthate to give the dithiocarbonate complex and a xanthate ester.²⁰

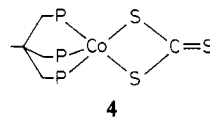
A similar scheme cannot be applied to the formation of **3**. One, in fact, could think that, when **1** is treated with alkoxide, the RO⁻ group may attack the coordinate Et₃P·CS₂ molecule to give the dithiocarbonate complex and phosphonium PR₄⁺ cations. This does not happen both because the presence of molecular oxygen in the reaction mixture is mandatory and because **3** can be obtained by means of other non-oxygen-containing nucleophiles such as RS⁻, S²⁻, and NR₂⁻. On the other hand, the dithiocarbonate complex **3** can be simply prepared by exposition in the air of a solution of **2**.

While at present no definitive conclusions are reached about the detailed mechanism and the role of oxygen in the formation of **3**, it appears reasonable that a fundamental step is the nucleophilic attack on the -CS₂ carbon atom to give products appropriate to substitutions at C1.

An experimental confirmation of this is the synthesis of the trithiocarbonate complex [(triphos)Co(S₂CS)] (**4**). This compound is obtained as red crystals from the reactions of **1** with alkoxides and elemental sulfur. It is air stable and soluble in common organic solvents in which it is nonconducting. The μ_{eff} at room temperature equal to 2.10 μ_{B} is indicative of one unpaired spin. The IR spectrum is identical with that of the dithiocarbonate derivative **3** except in the C=O region, where

3 adsorbs and in the C=S region, where **4** shows bands at 1040 and 855 cm⁻¹, which can be compared with those reported for some η^2 -coordinated CS₂ complexes.²¹ The UV spectrum in 1,2-dichloroethane is fully comparable with that of **3**, showing absorption maxima at 9700 ($\epsilon = 458$), 14 500 ($\epsilon = 430$), 18 500 ($\epsilon = 975$), and 20 850 cm⁻¹ ($\epsilon = 1815$).

All the information gathered from the spectroscopic, magnetic, and conductivity measurements is suggestive of a distorted square-pyramidal coordination around the cobalt atom, the three phosphorus atoms of the triphos ligand and two sulfur atoms of the trithiocarbonate ligand serving as donor atoms.



It is noteworthy that trithiocarbonate complexes have been obtained on reaction of CS₂ with metal carbonyl anions.²² Among the hypotheses about the formation of these products is included the presence of elemental sulfur released in some manner from CS₂ in the reaction mixture. To our knowledge the detailed mechanism for these reactions is not yet understood.

Electron withdrawal by the metal ion, besides facilitating attack by a nucleophile on the C1 carbon atom, can weaken the P-CS₂ bond. Recently, in fact, it has been reported that both PEt₃ and CS₂ complexes can be obtained by reaction of the Et₃P·CS₂ zwitterion with metal species.^{2,5} In this finding it is not completely surprising that **1** reacts with sodium to give the complex [(triphos)Co(π -CS₂)] (**5**) recently prepared in this laboratory by a different reaction.²³ However, it is interesting that, upon cleavage of the P-CS₂ bond, the CS₂ group rearranges to an η^2 complex. This may open a new route to CS₂ metal complex.

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Supplementary Material Available: Table IV, containing the least-squares plane related to the CoS₂CO group, and a listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

(18) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, A. *J. Am. Chem. Soc.* **1980**, *102*, 3847.

(19) Lin, I. J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394.

(20) Alison, J. M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 254.

(21) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 402 and references therein.

(22) Benson, I. B.; Hunt, J.; Knox, S. A. R.; Oliphant, V. *J. Chem. Soc., Dalton Trans.* **1978**, 1240.

(23) Bianchini, C.; Mealli, C.; Meli, A.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1980**, *19*, 2968.